13.3: Finding the pH of weak Acids, Bases, and Salts

The numerical examples and the images in this section have some problems (⬜ source text with comments).

> **◑ Learning Objectives**
>
> Make sure you thoroughly understand the following essential concepts that have been presented above.
>
> - Explain the difference between the terms C_a and [HA] as they relate to an aqueous solution of the acid HA.
> - Define *degree of dissociation* and sketch a plot showing how the values of $alpha$ for a conjugate pair HA and A$^-$ relate to each other and to the pK_a.
> - Derive *the relationship between* acid concentration and dissociation constant to the hydrogen ion concentration in a solution of a weak acid.
> - Re-write the above relation in *polynomial form*.
> - *Derive the approximation* that is often used to estimate the pH of a solution of a weak acid in water.
> - *Calculate the pH* of a solution of a weak monoprotic weak acid or base, employing the *"five-percent rule"* to determine if the approximation 2-4 is justified.
> - Predict whether an aqueous *solution of a salt* will be acidic or alkaline, and explain why by writing an appropriate equation.
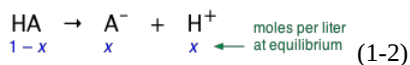
Most acids are weak; there are hundreds of thousands of them, whereas there are fewer than a dozen strong acids. We can treat weak acid solutions in much the same general way as we did for strong acids. The only difference is that we must now take into account the incomplete "dissociation"of the acid. We will start with the simple case of the pure acid in water, and then go from there to the more general one in which salts of the acid are present. The latter mixtures are known as buffer solutions and are extremely important in chemistry, physiology, industry and in the environment. To keep our notation as simple as possible, we will refer to "hydrogen ions" and [H$^+$] for brevity, and, wherever it is practical to do so, will assume that the acid HA "ionizes" or "dissociates" into H$^+$ and its conjugate base A$^-$.

1 Aqueous solutions of weak acids or bases

A weak acid (represented here as HA) is one in which the reaction

$$HA \rightleftharpoons A^- + H^+ \tag{13.3.1}$$

is incomplete. This means that if we add 1 mole of the pure acid HA to water and make the total volume 1 L, the equilibrium concentration of the conjugate base A$^-$ will be smaller (often *much* smaller) than 1 M/L, while that of undissociated HA will be only slightly less than 1 M/L. Equation 13.3.1 tells us that dissociation of a weak acid HA in pure water yields identical concentrations of its conjugate species. Let us represent these concentrations by *x*. Then, in our "1 M" solution, the concentration of each species is as shown here:

$$\begin{array}{ccccc} \text{HA} & \rightarrow & \text{A}^- & + & \text{H}^+ \\ 1-x & & x & & x \end{array} \quad \text{moles per liter at equilibrium} \tag{1-2}$$

When dealing with problems involving acids or bases, bear in mind that when we speak of "the concentration", we usually mean the *nominal* or *analytical* concentration which is commonly denoted by C_a. For example, for a solution made by combining 0.10 mol of pure formic acid HCOOH with sufficient water to make up a volume of 1.0 L, C_a = 0.10 M. However, we know that the concentration of the actual species [HCOOH] will be smaller the 0.10 M because some it ends up as the formate ion HCOO$^-$. It will, of course, always be the case that the sum

$$[HCOOH] + [HCOO^-] = C_a$$

For the general case of an acid HA, we can write a *mass balance equation*

$$C_a = [HA] + [A^-] \tag{13.3.2}$$

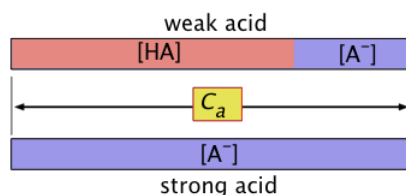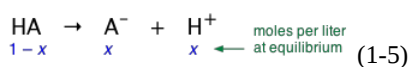which reminds us the "A" part of the acid must always be somewhere!

Figure 13.3.1: For a *strong acid* such as hydrochloric, its total dissociation means that [HCl] = 0, so the mass balance relationship in Equation 13.3.2 reduces to the trivial expression C_a = [Cl-]. Any acid for which [HA] > 0 is by definition a weak acid.

Similarly, for a base B we can write

$$C_b = [B] + [HB^+] \tag{13.3.3}$$

Equilibrium concentrations of the acid and its conjugate base

According to the above equations, the equilibrium concentrations of A^- and H^+ will be identical (as long as the acid is not so weak or dilute that we can neglect the small quantity of H^+ contributed by the autoprotolysis of H_2O). Let us represent these concentrations by x. Then, in a solution containing 1 M/L of a weak acid, the concentration of each species is as shown here:

$$\begin{array}{cccc} \text{HA} & \rightarrow & \text{A}^- & + & \text{H}^+ \\ 1-x & & x & & x \end{array} \leftarrow \text{moles per liter at equilibrium} \tag{1-5}$$

Substituting these values into the equilibrium expression for this reaction, we obtain

$$\frac{[A^-][H^+]}{[HA]} = \frac{x^2}{1-x} \tag{13.3.4}$$

In order to predict the pH of this solution, we must solve for x. The presence of terms in both x and x^2 here tells us that this is a quadratic equation. In most practical cases in which K_a is 10^{-4} or smaller, we can assume that x is much smaller than 1 M, allowing us to make the simplifying approximation

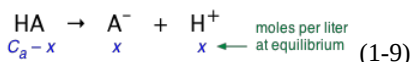$$(1-x) \approx 1 \tag{13.3.5}$$

so that

$$x^2 \approx K_a$$

and thus

$$x = \sqrt{K_a} \tag{13.3.6}$$

This approximation will not generally be valid when the acid is **very weak** or **very dilute.**

Solutions of arbitrary concentration

The above development was for a solution made by taking 1 mole of acid and adding sufficient water to make its volume 1.0 L. In such a solution, the nominal concentration of the acid, denoted by C_a, is 1 M.

We can easily generalize this to solutions in which C_a has any value:

$$\begin{array}{cccc} \text{HA} & \rightarrow & \text{A}^- & + & \text{H}^+ \\ C_a - x & & x & & x \end{array} \leftarrow \text{moles per liter at equilibrium} \tag{1-9}$$

The above relation is known as a "mass balance on A". It expresses the simple fact that the "A" part of the acid must always be *somewhere* — either attached to the hydrogen, or in the form of the hydrated anion A^-.

The corresponding equilibrium expression is

$$\frac{[H^+][A^-]}{[HA]} = \frac{x^2}{(C_a - x)} = K_a \tag{13.3.7}$$

and the approximations (when justified) Equation ??? and ??? become

$$(C_a - x) \approx C_a \tag{13.3.8}$$

$$x \approx \sqrt{C_a K_a} \tag{13.3.9}$$

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✔ Example 13.3.1: Aproximate pH of an Acetic Acid Solution

Estimate the pH of a 0.20 M solution of acetic acid, $K_a = 1.8 \times 10^{-5}$.

Solution

For brevity, we will represent acetic acid CH_3COOH as HAc, and the acetate ion by Ac^-. As before, we set x = $[H^+]$ = $[Ac^-]$, neglecting the tiny quantity of H^+ that comes from the dissociation of water.

$$\frac{[H^+][Ac^-]}{[HAc]} = \frac{x^2}{(1-x)}$$

Substitution into the equilibrium expression yields

$$\frac{x^2}{(0.20-x)} = 1.8 \times 10^{-5}$$

The rather small value of K_a suggests that we can drop the x term in the denominator, so that

$$\frac{x^2}{0.20} \approx 1.8 \times 10^{-5}$$

or

$$x \approx \sqrt{(0.20)(1.8 \times 10^{-5})} = 1.9 \times 10^{-3} \ M$$

The pH of the solution is

$$-\log(1.9 \times 10^{-3}) = 2.7$$

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Degree of dissociation

Even though we know that the process $HA \rightarrow H^+ + A^-$ does not correctly describe the transfer of a proton to H_2O, chemists still find it convenient to use the term "ionization" or "dissociation". The "degree of dissociation" (denoted by α of a weak acid is just the fraction

$$\alpha = \frac{[A^-]}{C_a} \tag{13.3.10}$$

which is often expressed as a per cent ($\alpha \times 100$).

Degree of dissociation depends on the concentration

It's important to understand that whereas K_a for a given acid is essentially a constant, α *will depend on the concentration* of the acid. Note that these equations are also valid for weak bases if K_b and C_b are used in place of K_a and C_a.

This can be shown by substituting Eq 5 into the expression for K_a:

$$K_a = \frac{C_a \alpha^2}{1 - \alpha} \tag{1-14}$$

Solving this for α results in a quadratic equation, but if the acid is sufficiently weak that we can say $(1 - \alpha) \approx 1$, the above relation becomes

$$\alpha \approx \sqrt{K_a / C_a} \tag{1-15}$$

the amount of HA that dissociates varies inversely with the square root of the concentration; as C_a approaches zero, α approaches unity and [HA] approaches C_a.

This principle is an instance of the *Ostwald dilution law* which relates the dissociation constant of a weak electrolyte (in this case, a weak acid), its degree of dissociation, and the concentration.

A common, but incorrect explanation of this law in terms of the Le Chatelier principle states that dilution increases the concentration of water in the equation $HA + H_2O \rightarrow H_3O^+ + A^-$, thereby causing this equilibrium to shift to the right. The error here is that $[H_2O]$ in most aqueous solutions is so large (55.5 M) that it can be considered constant; this is the reason the $[H_2O]$ term does not appear in the expression for K_a. Another common explanation is that dilution reduces $[H_3O^+]$ and $[A^-]$, thus shifting the dissociation process to the right. However, dilution similarly reduces $[HA]$, which would shift the process to the left. In fact, these two processes compete, but the former has greater effect because two species are involved.

It is probably more satisfactory to avoid Le Chatelier-type arguments altogether, and regard the dilution law as an entropy effect, a consequence of the greater dispersal of thermal energy throughout the system. This energy is carried by the molecular units within the solution; dissociation of each HA unit produces two new particles which then go their own ways, thus spreading (or "diluting") the thermal energy more extensively and massively increasing the number of energetically-equivalent microscopic states, of which entropy is a measure. (More on this here)

Degree of dissociation depends on the pH

Plots of this kind are discussed in more detail in the next lesson in this set under the heading ionization fractions.
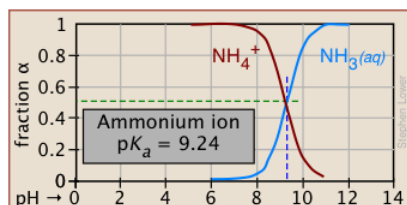
The Le Chatelier principle predicts that the extent of the reaction

$$HA \rightarrow H^+ + A^-$$

will be affected by the hydrogen ion concentration, and thus by the pH. This is illustrated here for the ammonium ion. Notice that when the pH is the same as the pK_a, the concentrations of the acid- and base forms of the conjugate pair are identical.

✔ **Example 13.3.1: percent dissociation**

A 0.75 M solution of an acid HA has a pH of 1.6. What is its percent dissociation?

Solution

The dissociation stoichiometry $HA \rightarrow H^+ + AB^-$ tells us the concentrations $[H^+]$ and $[A^-]$ will be identical. Thus $[H^+] = 10^{-1.6} = 0.025$ M $= [A^-]$. The dissociation fraction

$$\alpha = \frac{[A^-]}{[HA]} = \frac{0.025}{0.75} = 0.033$$

and thus the acid is **3.3%** dissociated at 0.75 M concentration.

Sometimes the percent dissociation is given, and K_a must be evaluated.

✔ **Example 13.3.3: Ka from degree of dissociation**

A weak acid HA is 2 percent dissociated in a 1.00 M solution. Find the value of K_a.

Solution

The equilibrium concentration of HA will be 2% smaller than its nominal concentration, so $[HA] = 0.98$ M, $[A^-] = [H^+] = 0.02$ M. Substituting these values into the equilibrium expression gives

$$\frac{[H^+][A^-]}{[HA]} = \frac{.0004}{.98} = 4.01 \times 10^{-4}$$

"Concentration of the acid" and [HA] are not the same

When dealing with problems involving acids or bases, bear in mind that when we speak of "the concentration", we usually mean the *nominal* or *analytical* concentration which is commonly denoted by C_a.

So for a solution made by combining 0.10 mol of pure formic acid HCOOH with sufficient water to make up a volume of 1.0 L, C_a = 0.10 *M*. However, we know that the concentration of the actual species [HCOOH] will be smaller the 0.10 M because some it ends up as the formate ion HCOO⁻. However, it will always be the case that the sum

[HCOOH] + [HCOO⁻] = C_a.

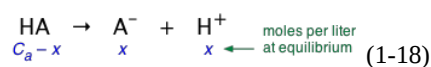For the general case of an acid HA, we can write a *mass balance equation*

C_a = [HA] + [A⁻](1-16)

which reminds us the "A" part of the acid must always be somewhere!

Similarly, for a base B we can write

C_b = [B] + [HB⁺](1-17)

Degree of dissociation varies inversely with the concentration

If we represent the dissociation of a C_a *M* solution of a weak acid by

$$HA \rightarrow A^- + H^+$$
$$C_a - x \quad\quad x \quad\quad x \leftarrow \text{moles per liter at equilibrium} \quad (1\text{-}18)$$

then its dissociation constant is given by

$$K_a = \frac{x^2}{C_a - x} \quad (1\text{-}19)$$

Because the C_a term is in the denominator here, we see that the amount of HA that dissociates varies inversely with the concentration; as C_a approaches zero, [HA] approaches C_a.

If we represent the fraction of the acid that is dissociated as

$$\alpha = \frac{[A^-]}{C_a} \quad (1\text{-}20)$$

then Eq 8 becomes

$$K_a = \frac{C_a \alpha^2}{1 - \alpha} \quad (1\text{-}21)$$

If the acid is sufficiently weak that *x* does not exceed 5% of C_a, the α-term in the denominator can be dropped, yielding

$K_a \approx C_a \alpha^2$ (1-22)

Note that the above equations are also valid for weak bases if Kb and C_b are used in place of K_a and C_a.

> ### ✔ Example 13.3.1: effects of dilution
>
> Compare the percent dissociation of 0.10 M and .0010 M solutions of boric acid ($K_a = 3.8 \times 10^{-10}$).
>
> **Solution**
> Boric acid is sufficiently weak that we can use the approximation of Eq 1-22 to calculate a: α = (5.8E–10 / .1)^½ = 7.5E-5; multiply by 100 to get .0075 % diss. For the more dilute acid, a similar calculation yields 7.6E–4, or 0.76%.

2 Carrying out acid-base calculations

In Problem Example 1, we calculated the pH of a monoprotic acid solution, making use of an approximation in order to avoid the need to solve a quadratic equation. This raises the question: how "exact" must calculations of pH be? It turns out that the relation

between pH and the nominal concentration of an acid, base, or salt (and especially arbitrary mixtures of these) can become quite complicated, requiring the solution of sets of simultaneous equations.

However, for almost all practical applications, one can make some approximations that simplify the math without detracting significantly from the accuracy of the results.
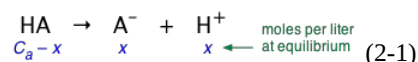
Equilibrium constants are rarely exactly known

As we pointed out in the preceding lesson, the "effective" value of an equilibrium constant (the *activity*) will generally be different from the value given in tables in all but the most dilute ionic solutions. Even if the acid or base itself is dilute, the presence of other "spectator" ions such as Na^+ at concentrations much in excess of 0.001 M can introduce error.

The usual advice is to consider K_a values to be accurate to ±5 percent at best, and even more uncertain when total ionic concentrations exceed 0.1 M. As a consequence of this uncertainty, there is generally little practical reason to express the results of a pH calculation to more than two significant digits.

Finding the pH of a solution of a weak monoprotic acid

This is by far the most common type of problem you will encounter in a first-year Chemistry class. You are given the concentration of the acid, expressed as C_a moles/L, and are asked to find the pH of the solution. The very important first step is to make sure you understand the problem by writing down the equation expressing the concentrations of each species in terms of a single unknown, which we represent here by x:

$$HA \rightarrow \underset{x}{A^-} + \underset{x}{H^+} \quad \overset{\text{moles per liter}}{\underset{\text{at equilibrium}}{\longleftarrow}} \quad (2\text{-}1)$$
$$\underset{C_a-x}{}$$

Substituting these values into the expression for K_a, we obtain

$$\frac{[H^+]\,[A^-]}{[HA]} = \frac{x^2}{(C_a-x)} = K_a \quad (2\text{-}2)$$

Don't bother to memorize these equations! If you understand the concept of mass balance on "A" expressed in (2-1), and can write the expression for K_a, you just substitute the x's into the latter, and you're off! If you feel the need to memorize stuff you don't need, it is likely that you don't really understand the material — and that should be a *real* worry!

In order to predict the pH of this solution, we must first find $[H^+]$, that is, x. The presence of terms in both x and x^2 here tells us that this is a quadratic equation. This can be rearranged into $x^2 = K_a\,(1 - x)$ which, when written in standard polynomial form, becomes the quadratic

$$[H^+]^2 - C_a[H^+] - K_w = 0 \qquad (13.3.11)$$

However, don't panic! As we will explain farther on, in most practical cases we can make some simplifying approximations which eliminate the need to solve a quadratic. And when, as occasionally happens, a quadratic is unavoidable, we will show you some relatively painless ways of dealing with it.

How to deal with Quadratic Equations

What you do will depend on what tools you have available. If you are only armed with a simple calculator, then there is always the venerable quadratic formula that you may have learned about in high school, but if at all possible, you should avoid it: its direct use in the present context is somewhat laborious and susceptible to error.

Use of the standard quadratic formula on a computer or programmable calculator can lead to weird results!

The reason for this is that if $b^2 >> |4ac|$, one of the roots will require the subtraction of two terms whose values are very close; this can lead to considerable error when carried out by software that has finite precision.

One can get around this by computing the quantity

$$Q = -\frac{b + \pm(b)\sqrt{b^2 - 4ac}}{2}$$

from which the roots are $x_1 = Q/a$ and $x_2 = c/Q$. (See any textbook on numerical computing for more on this and other methods.)

However, who want's to bother with this stuff in order to solve typical chemistry problems? Better to avoid quadratics altogether if at all possible!

Remember: there are always *two* values of *x* (two *roots*) that satisfy a quadratic equation. For all acid-base equilibrium calculations that are properly set up, these roots will be *real*, and only one will be positive; this is the one you take as the answer.

Approximations, judiciously applied, simplify the math

We have already encountered two of these approximations in the examples of the preceding section:

1. In all but the most dilute solutions, we can assume that the dissociation of the acid HA is the sole source of H$^+$, with the contribution due to water autoprotolysis being negligible.
2. We were able to simplify the equilibrium expressions by assuming that the *x*-term, representing the quantity of acid dissociated, is so small compared to the nominal concentration of the acid C_a that it can be neglected. Thus in Problem Example 1, the term in the denominator that has the form (0.1 - *x*) , representing the equilibrium concentration of the undissociated acid, is replaced by 0.1.

Most people working in the field of practical chemistry will never encounter situations in which the first of these approximations is invalid. This is not the case, however, for the second one.

Should I drop the *x*, or forge ahead with the quadratic form?

If the acid is fairly concentrated (usually with $C_a > 10^{-3}$ M) and sufficiently weak that most of it remains in its protonated form HA, then the concentration of H$^+$ it produces may be sufficiently small that the expression for K_a reduces to

$K_a \approx [H^+]^2 / C_a$

so that

$[H^+] \approx (K_a C_a)^{\frac{1}{2}}$(2-4)

This can be a great convenience because it avoids the need to solve a quadratic equation. However, it also exposes you to the danger that this approximation may not be justified.

The usual advice is that if this first approximation of *x* exceeds 5 percent of the value it is being subtracted from (0.10 in the present case), then the approximation is *not* justified. We will call this the "five percent rule".

> ✔ Example 13.3.5:
>
> **Problem Example 5 - pH and degree of dissociation**
>
> a. Estimate the pH of a 0.20 M solution of acetic acid, $K_a = 1.8 \times 10^{-5}$.
> b. What percentage of the acid is dissociated?
>
> *Solution*
>
> For brevity, we will represent acetic acid CH$_3$COOH as HAc, and the acetate ion by Ac$^-$. As before, we set x = [H$^+$] = [Ac$^-$], neglecting the tiny quantity of H$^+$ that comes from the dissociation of water.
>
> Substitution into the equilibrium expression yields
>
> \[K_a = x^2/(0.20 - x)
>
> Can we simplify this by applying the approximation 0.20 – x ≈ 0.20 ? Looking at the number on the right side of this equation, we note that it is quite small. This means the left side must be equally small, which requires that the denominator be fairly large, so we can probably get away with dropping x. Doing so yields
>
> (x^2 / 0.20) = 1.8E-5 or x = (0.20 × 1.8E–5)$^{\frac{1}{2}}$ = 1.9E-3 M
>
> The "5 per cent rule" requires that the above result be no greater than 5% of 0.20, or 0.010. Because 0.0019 meets this condition, we can set
> x = [H$^+$] ≈ 1.9 × 10^{-3} M, and the pH will be –log (1.9 × 10^{-3}) = **2.7**

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b) Percent dissociation: $100\% \times (1.9 \times 10^{-3} \text{ M}) / (0.20 \text{ M}) =$ **0.95%**

This plot shows the combinations of K_a and C_a that generally yield satisfactory results with the approximation of Eq 4.

Weak bases are treated in an exactly analogous way:

> ✔ Example 13.3.1: Weak base
>
> Methylamine CH_3NH_2 is a gas whose odor is noticed around decaying fish. A solution of CH_3NH_2 in water acts as a weak base. A 0.10 M solution of this amine in water is found to be 6.4% ionized. Use this information to find \Kb and pK_b for methylamine.
>
> ***Solution:*** When methylamine "ionizes", it takes up a proton from water, forming the methylaminium ion:
>
> $CH_3NH_2 + H_2O \rightarrow CH_3NH_3^+ + OH^-$
>
> Let $x = [CH_3NH_3^+] = [OH^-] = .064 \times 0.10 = 0.0064$
>
> $[CH_3NH_2] = (0.10 - .064) = 0.094$
>
> Substitute these values into equilibrium expression for \Kb:
>
> $$K_b = \frac{0.0064^2}{0.094}$$
>
> To make sure we can stop here, we note that (3.6E4 / .01) = .036; this is smaller than .05, so we pass the 5% rule and can use the approximation and drop the
> x-term in the denominator.
>
> $pK_b = -\log \text{\Kb} = -\log (4.4 \times 10^{-10}) =$ **3.36**

However, one does not always get off so easily!

> ✔ Example 13.3.6: pH of a chloric acid solution
>
> With a K_a of 0.010, $HClO_2$ is one of the "stronger" weak acids, thanks to the two oxygen atoms whose electronegativity withdraws some negative charge from the chlorine atom, making it easier for the hydrogen to depart as a proton.
>
> Find the pH of a 0.10 M solution of chloric acid in pure water.
>
> $$0.010 = \frac{x^2}{0.10 - x}$$
>
> (i)
>
> The approximation $0.10 - x \approx 0.10$ gives us
>
> $x \approx (K_a C_a)^{\frac{1}{2}} = (0.010 \times 0.10)^{\frac{1}{2}} = (.001)^{\frac{1}{2}} = .032$ (ii)
>
> The difficulty, in this case, arises from the numerical value of K_a differing from the nominal concentration 0.10 M by only a factor of 10. As a result,
> $x / C_a = .032 / 0.10 = 0.32$ which clearly exceeds the 5% limit; we have no choice but to face the full monte of the quadratic solution. (see Problem Example 8 below).

Successive approximations will get you there with minimal math

In the *method of successive approximations*, you start with the value of $[H^+]$ (that is, x) you calculated according to (2-4), which becomes the first approximation. You then substitute this into (2-2), which you solve to get a second approximation. This cycle is repeated until differences between successive answers become small enough to ignore.

✔ **Example 13.3.1: Method of successive approximations**

Estimate the pH of a 0.10 M aqueous solution of $HClO_2$, K_a = 0.010, using the method of successive approximations.

Solution: The equilibrium condition is

$$K_a = \frac{x \cdot x}{c_a - x}$$

We solve this for x (neglecting the x in the denominator), resulting in the first approximation x_1, and then successively plug each result into the previous equation, yielding approximations x_2 and x_3:

$$x_1 = \sqrt{K_a \cdot c_a} = 0.032$$

$$x_2 = \sqrt{K_a \cdot (c_a - x_1)} = 0.026$$

$$x_3 = \sqrt{K_a \cdot (c_a - x_2)} = 0.027$$

The last two approximations x_2 and x_3 are within 5% of each other.

Note that if we had used x_1 as the answer, the error would have been 18%.

(An exact numeric solution yields the roots 0.027016 and –0.037016)

Use a graphic calculator or computer to find the positive root

The real roots of a polynomial equation can be found simply by plotting its value as a function of one of the variables it contains.

In this example, the pH of a 10^{-6} M solution of hypochlorous acid (HOCl, K_a = 2.9E–8) was found by plotting the value of $y = ax^2 + bx + c$, whose roots are the two values of x that correspond to $y = 0$.

This method generally requires a bit of informed trial-and-error to make the locations of the roots visible within the scale of the axes.

Be lazy, and use an on-line quadratic equation solver

If you google "quadratic equation solver", you will find numerous on-line sites that offer quick-and-easy "fill-in-the-blanks" solutions.

Unfortunately, few of these will be useful for acid-base problems involving numbers that must be expressed in "E-notation" (*e.g.*, 2.7E-11.) Of those that do, the one at the MathIsFun site is highly recommended; others can be found here and at the Quad2Deg site.

If you can access a quad equation solver on your personal electronic device or through the Internet, this is quick and painless. All you need to do is write the equation in polynomial form $ax^2 + bx + c = 0$, insert values for a, b, and c, and away you go!

This is so easy, that many people prefer to avoid the "5% test" altogether, and go straight to an exact solution. *However, make sure can do the 5%-thing for exams where Internet-accessible devices are not permitted!*

✔ **Example 13.3.1: chloric acid, again**

Estimate the pH of a 0.10 M aqueous solution of $HClO_2$, K_a = 0.010.

Solution

The reaction equation $HClO_2 \rightarrow H^+ + ClO_2-$ defines the equilibrium expression

$$0.010 = \frac{x \cdot x}{0.10 - x}$$

Multiplying by the denominator yields

$x^2 = 0.010 \times (0.10 - x) = .0010 - .01\,x$ which we arrange into standard polynomial form:

$x^2 + 0.01\,x - 0.0010 = 0$

Entering the coefficients {1 .01 –.001} into an online quad solver yields the roots
.027 and –.037. Taking the positive one, we have $[H^+]$ = .027 M;
the solution pH is $-\log$ .027 = **1.6**.

Note: a common error is to forget to enter the minus sign for the last term; try doing this and watch the program blow up!

Avoid math altogether and make a log-C vs pH plot

This is not only simple to do (all you need is a scrap of paper and a straightedge), but it will give you far more insight into what's going on, especially in polyprotic systems. All explained in Section 3 of the next lesson.

Solutions of salts

Most salts do *not* form pH-neutral solutions

Salts such as sodium chloride that can be made by combining a strong acid (HCl) with a strong base (NaOH, KOH) have a neutral pH, but these are exceptions to the general rule that solutions of most salts are mildly acidic or alkaline.

Salts of a strong base and a weak acid yield alkaline solutions.

"Hydro-lysis" literally means "water splitting", as exemplified by the reaction $A^- + H_2O \rightarrow HA + OH^-$. The term describes what was believed to happen prior to the development of the Brønsted-Lowry proton transfer model.

This important property has historically been known as *hydrolysis* — a term still used by chemists.
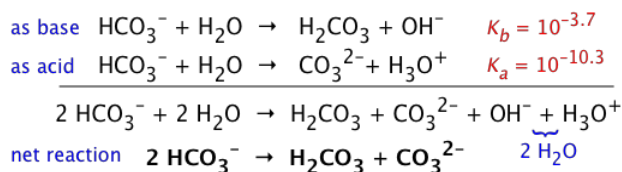
Some examples:

Potassium Cyanide

KCN can be thought of the salt made by combining the strong base KOH with the weak acid HCN: $K^+ + OH^- \rightarrow KOH$. When solid KCN dissolves in water, this process is reversed, yielding a solution of the two ions. K^+, being a "strong ion", does not react with water. However, the "weak ion" CN^-, being the conjugate base of a weak acid, will have a tendency to abstract protons from water: $CN^- + H_2O \rightarrow HCN + OH^-$, causing the solution to remain slightly alkaline.

Sodium bicarbonate

$NaHCO_3$ (more properly known as sodium hydrogen carbonate) dissolves in water to yield a solution of the hydrogen carbonate ion HCO_3^-. This ion is an *ampholyte* — that is, it is both the conjugate base of the weak carbonic acid H_2CO_3, as well as the conjugate acid of the carbonate ion CO_3^{2-}:

$$[Gly^-] = \frac{10^{-9.8} \times 0.10}{[H^+]} = 10^{-4.7}$$

The HCO_3^- ion is therefore *amphiprotic*: it can both accept and donate protons, so both processes take place:

$$
\begin{array}{lll}
\text{as base} & HCO_3^- + H_2O \rightarrow H_2CO_3 + OH^- & K_b = 10^{-3.7} \\
\text{as acid} & HCO_3^- + H_2O \rightarrow CO_3^{2-} + H_3O^+ & K_a = 10^{-10.3} \\
\hline
& 2\,HCO_3^- + 2\,H_2O \rightarrow H_2CO_3 + CO_3^{2-} + OH^- + H_3O^+ & \\
\text{net reaction} & \mathbf{2\,HCO_3^- \rightarrow H_2CO_3 + CO_3^{2-}} & 2\,H_2O
\end{array}
$$

However, if we compare the K_a and K_b of HCO_3^-, it is apparent that its basic nature wins out, so a solution of $NaHCO_3$ will be slightly alkaline. (The value of pK_b is found by recalling that $K_a + K_b = 14$.)

Sodium acetate

A solution of CH_3COONa serves as a model for the strong-ion salt of any organic acid, since all such acids are weak:
$CH_3COO^- + H_2O \rightarrow CH_3COOH + OH^-$
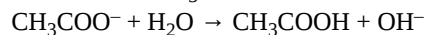
Salts of most cations (positive ions) give acidic solutions

The protons can either come from the cation itself (as with the ammonium ion NH_4^+), or from waters of hydration that are attached to a metallic ion.

This latter effect happens with virtually all salts of metals beyond Group I; it is especially noticeable for salts of transition ions such as hexaaquoiron(III) ("ferric ion"):

$$Fe(H_2O)_6^{3+} \rightarrow Fe(H_2O)_5OH^{2+} + H^+ \quad (2\text{-}5)$$
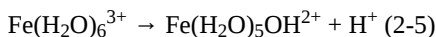
This comes about because the positive field of the metal enhances the ability of H_2O molecules in the hydration shell to lose protons. In the case of the hexahyrated ion shown above, a whose succession of similar steps can occur, but for most practical purposes only the first step is significant.

> ✔ **Example 13.3.10: Aluminum chloride solution**
>
> Find the pH of a 0.15 M solution of aluminum chloride.
>
> **Solution**
>
> The aluminum ion exists in water as hexaaquoaluminum $Al(H_2O)_6^{3+}$, whose $pK_a = 4.9$, $K_a = 10^{-4.9} = 1.3E\text{-}5$. Setting $x = [H^+] = [Al(H_2O)_5OH^{2+}]$, the equilibrium expression is
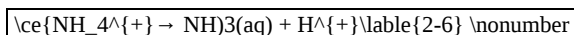>
> $$[Gly^-] = \frac{10^{-9.8} \times 0.10}{[H^+]} = 10^{-4.7}$$
>
> Using the above approximation, we get
> $x \approx (1.96E\text{-}6)^{\frac{1}{2}} = 1.4E\text{-}3$, corresponding to **pH = 2.8**.
>
> Finally, we compute $x/C_a = 1.4E\text{-}3 \div 0.15 = .012$ confirming that we are within the "5% rule".

The only commonly-encountered salts in which the proton is donated by the cation itself are those of the *ammonium ion*:

$$\boxed{\ce{NH_4^{+} → NH)3(aq) + H^{+}}\lable{2-6} \nonumber}$$

> ✔ **Example 13.3.11: Ammonium chloride solution**
>
> Calculate the pH of a 0.15 M solution of NH4Cl. The ammonium ion K_a is 5.5E–10.
>
> **Solution**
>
> According to Eq 6 above, we can set $[NH3] = [H^+] = x$, obtaining the same equilibrium expression as in the preceding problem.
>
> Because K_a is quite small, we can safely use the approximation $0.15 - 1 \approx .015$, which yields pH = –log 0.90E–5 = **5.0**

Most salts of weak acids form alkaline solutions

As indicated in the example, such equilibria strongly favor the left side; the stronger the acid HA, the less alkaline the salt solution will be.

Because an ion derived from a weak acid such as HF is the conjugate base of that acid, it should not surprise you that a salt such as NaF forms an alkaline solution, even if the equilibrium greatly favors the left side::

$$F^- + H_2O \rightleftharpoons HF + OH^- \quad (2\text{-}7)$$

> ✔ **Example 13.3.1:**
>
> **Solution of sodium fluoride**
>
> Find the pH of a 0.15 M solution of NaF. (HF $K_a = 6.7E\text{-}4$)
>
> ***Solution:*** The reaction is F- + H_2O = HF + OH^-; because HF is a weak acid, the equilibrium strongly favors the right side. The usual approximation yields
>
> $$[Gly^-] = \frac{10^{-9.8} \times 0.10}{[H^+]} = 10^{-4.7}$$

However, on calculating x/C_a = .01 ÷ 0.15 = .07, we find that this does not meet the "5% rule" for the validity of the approximation. We therefore expand the equilibrium expression

$$[Gly^-] = \frac{10^{-9.8} \times 0.10}{[H^+]} = 10^{-4.7}$$

into standard polynomial form x^2 + 6.7E–4 x – 1.0E–4 = 0 and enter the coefficients {1 6.7E–4 –.0001} into a quadratic solver. This yields the positive root x = 0.0099 which turns out to be sufficiently close to the approximation that we could have retained it after all.. perhaps 5% is a bit too restrictive for 2-significant digit calculations!

What about a salt of a weak acid *and* a weak base?

A salt of a weak acid gives an alkaline solution, while that of a weak base yields an acidic solution. What happens if we dissolve a salt of a weak acid and a weak base in water? Ah, this can get a bit tricky! Nevertheless, this situation arises very frequently in applications as diverse as physiological chemistry and geochemistry.

As an example of how one might approach such a problem, consider a solution of ammonium formate, which contains the ions NH_4^+ and HCOO-. Formic acid, the simplest organic acid, has a pK_a of 3.7; for NH_4^+, pK_a = 9.3.

Three equilibria involving these ions are possible here; in addition to the reactions of the ammonium and formate ions with water, we must also take into account their tendency to react with each other to form the parent neutral species:

$NH_4^+ \rightarrow NH_3 + H^+$	$K_1 = 10^{-9.3}$
$HCOO^- + H_2O \rightarrow HCOOH + OH^-$	$K_2 = (1O^{-14}/10^{-3.7}) = 10^{-10.3}$
$NH_4^+ + HCOO^- \rightarrow NH_3 + HCOOH$	K_3

Inspection reveals that the last equation above is the sum of the first two, plus the reverse of the dissociation of water

$H^+ + OH^- \rightarrow H_2O$	$K_4 = 1/K_w$

The value of K_3 is therefore

$$[Gly^-] = \frac{10^{-9.8} \times 0.10}{[H^+]} = 10^{-4.7} \qquad (2\text{-}8)$$

A rigorous treatment of this system would require that we solve these equations simultaneously with the charge balance and the two mass balance equations. However, because K_3 is several orders of magnitude greater than K_1 or K_2, we can greatly simplify things by neglecting the other equilibria and considering only the reaction between the ammonium and formate ions.

Notice that the products of this reaction will tend to suppress the extent of the first two equilibria, reducing their importance even more than the relative values of the equilibrium constants would indicate.

✔ Example 13.3.1:

ammonium formate

Estimate the pH of a 0.0100 M solution of ammonium formate in water.

Solution: From the stoichiometry of $HCOONH_4$,

$[NH_4^+] = [HCOO^-]$ and $[NH_3] = [HCOOH]$ (i)

then, from Eq 8 above,

$$K_3 = \frac{[NH_3][HCOOH]}{[NH_4^+][HCOO^-]} = \frac{[HCOOH]^2}{[HCOO^-]^2} = \frac{K_w}{K_a K_b} \quad (ii)$$

in which K_b is the base constant of ammonia, $K_w/10^{-9.3}$.

From the formic acid dissociation equilibrium we have

$$[Gly^-] = \frac{10^{-9.8} \times 0.10}{[H^+]} = 10^{-4.7} \quad (iii)$$

We now rewrite the expression for K_3

$$K_a = \frac{[\text{HCOOH}]^2}{[\text{HCOO}^-]^2} = \frac{[\text{H}^+]^2}{K_a{}^2} = \frac{K_w}{K_a K_b} \quad \text{(iv)}$$

which yields

$$[\text{Gly}^-] = \frac{10^{-9.8} \times 0.10}{[\text{H}^+]} = 10^{-4.7} \quad \text{(v)}$$
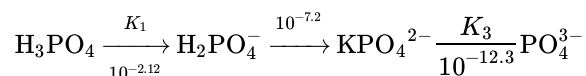
and thus the pH is **6.5**

What is interesting about this last example is that the pH of the solution is apparently independent of the concentration of the salt. If $K_a = K_b$, then this is always true and the solution will be neutral (neglecting activity effects in solutions of high ionic strength). Otherwise, it is only an approximation that remains valid as long as the salt concentration is substantially larger than the magnitude of either equilibrium constant. Clearly, the pH of any solution must approach that of pure water as the solution becomes more dilute.

Salts of analyte ions

Polyprotic acids form multiple anions; those that can themselves donate protons, and are thus amphiprotic, are called *analytes*. The most widely known of these is the *bicarbonate* (hydrogen carbonate) ion, HCO_3^-, which we commonly know in the form of its sodium salt NaHCO_3 as *baking soda*.

The other analyte series that is widely encountered, especially in biochemistry, is those derived from phosphoric acid:

$$\text{H}_3\text{PO}_4 \xrightarrow[10^{-2.12}]{K_1} \text{H}_2\text{PO}_4^- \xrightarrow{10^{-7.2}} \text{KPO}_4{}^{2-} \xrightarrow[10^{-12.3}]{K_3} \text{PO}_4^{3-}$$

The solutions of analyte ions we most often need to deal with are the of "strong ions", usually Na^+, but sometimes those of Group 2 cations such as Ca^{2+}.

The exact treatment of these systems is generally rather complicated, but for the special cases in which the successive K_a's of the parent acid are separated by several orders of magnitude (as in the two systems illustrated above), a series of approximations reduces the problem to the simple expression

$$\left[\text{H}^+\right] \approx \sqrt{K_1 K_2} \tag{13.3.12}$$

which, you will notice, as with the salt of a weak acid and a weak base discussed in the preceding subsection predicts that the pH is independent of the salt's concentration. This, of course, is a sure indication that this treatment is incomplete. Fortunately, however, it works reasonably well for most practical purposes, which commonly involve buffer solutions.

> 📌 Exact treatment of solutions of weak acids and bases
>
> When dealing with acid-base systems having very small K_a's, and/or solutions that are extremely dilute, it may be necessary to consider *all* the species present in the solution, including minor ones such as OH^-.
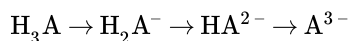>
> This is almost never required in first-year courses. However, for students in more advanced courses, this "comprehensive approach" (as it is often called) illustrates the important general methodology of dealing with more complex equilibrium problems. It also shows explicitly how making various approximations gradually simplifies the treatment of more complex systems.

Solutions of polyprotic acids

A diprotic acid H_2A can donate its protons in two steps:

$$\text{H}_2\text{A} \rightarrow \text{HA}^- \rightarrow \text{HA}^-$$

and similarly, for a tripotic acid H3A:

$$\text{H}_3\text{A} \rightarrow \text{H}_2\text{A}^- \rightarrow \text{HA}^{2-} \rightarrow \text{A}^{3-}$$

In general, we can expect K_a2 for the "second ionization" to be smaller than K_a1 for the first step because it is more difficult to remove a proton from a negatively charged species. The magnitude of this difference depends very much on whether the two removable protons are linked to the same atom, or to separate atoms spaced farther apart.

Some polyprotic acids you should know

These acids are listed in the order of decreasing K_{a1}. The numbers above the arrows show the successive K_a's of each acid.

- Notice how successive K_a's of each acid become smaller, and how their ratios relate to the structures of each acid.
- **Sulfuric acid** is the only *strong* polyprotic acid you are likely to encounter.
- **Sulfurous acid** has never been detected; what we refer to as H_2SO_3 is more properly represented as a hydrated form of sulfur dioxide: which dissociates into the hydrosulfite ion:
  $SO_2 \cdot H_2O \rightarrow HSO_3^- + H^+$. The ion HSO_3^- exists only in solution; solid bisulfite salts are not known.
- Similarly, pure **carbonic acid** has never been isolated, but it does exist as a minority species in an aqueous solution of CO_2: $[CO_2(aq)] = 650[H_2CO_3]$. The formula H_2CO_3 ordinarily represents the combination $CO_2(aq)$ and "true" H_2CO_3. The latter is actually about a thousand times stronger than is indicated by the pK_a of 6.3, which is the weighted average of the equilibrium mixture.
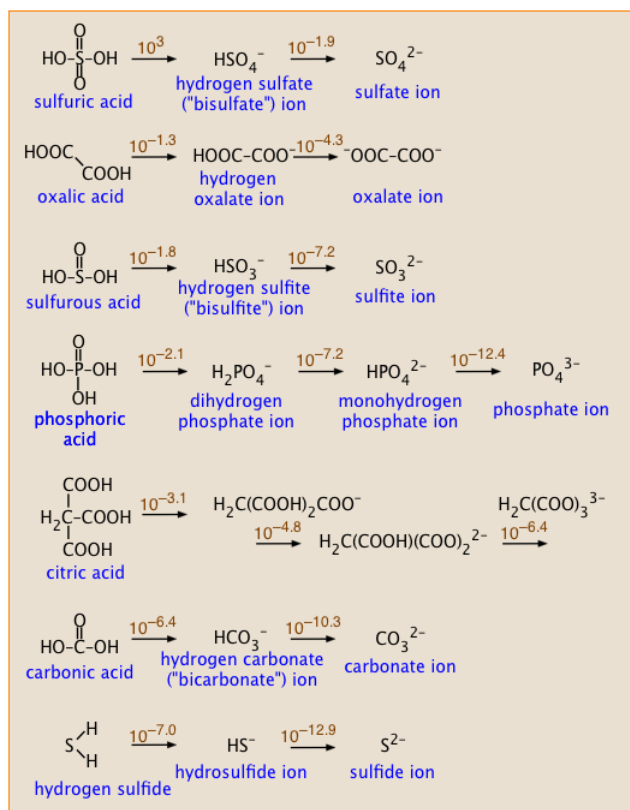
pH of a polyprotic acid (LindaHanson, 17 min)

✔ Example 13.3.1: Comparison of two diprotic acids

Compare the successive pK_a values of sulfuric and oxalic acids (see their structures in the box, above right), and explain why they should be so different.
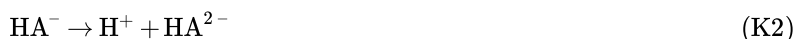
Solution

The two pK_a values of sulfuric acid differ by 3.0 − (−1.9) = 4.9, whereas for oxalic acid the difference is 1.3 − (−4.3) = 3.0. That's a difference of almost 100 between the two K_a's. Removal of a second proton from a molecule that already carries some negative charge is always expected to be less favorable energetically. In sulfuric acid, the two protons come from −OH groups connected to the same sulfur atom, so the negative charge that impedes loss of the second proton is more localized near the site

> of its removal. In oxalic acid, the two protons are removed from –OH groups attached to separate carbon atoms, so the negative charge of the mono-negative ions will exert less restraint on loss of the second proton.

Solutions of polyprotic acids in pure water

With the exception of sulfuric acid (and some other seldom-encountered strong diprotic acids), most polyprotic acids have sufficiently small K_{a1} values that their aqueous solutions contain significant concentrations of the free acid as well as of the various dissociated anions.

Thus for a typical diprotic acid H_2A, we must consider the three coupled equilibria

$$H_2A \rightarrow H^+ + HA^- \tag{K1}$$

$$HA^- \rightarrow H^+ + HA^{2-} \tag{K2}$$

$$H_2O \rightarrow H^+ + OH^- \tag{Kw}$$

> An exact treatment of such a system of four unknowns $[H_2A]$, $[HA^-]$, $[A^{2-}]$ and $[H^+]$ requires the solution of a quartic equation. If we include $[OH^-]$, it's even worse!

In most practical cases, we can make some simplifying approximations:

- Unless the solution is extremely dilute or K_1 (and all the subsequent K's) are extremely small, we can forget that any hydroxide ions are present at all.
- If K_1 is quite small, and the ratios of succeeding K's are reasonably large, we may be able, without introducing too much error, to neglect the other K's and treat the acid as monoprotic.

In addition to the three equilibria listed above, a solution of a polyprotic acid in pure water is subject to the following two conditions:

Material balance: although the distribution of species between the acid form H_2A and its base forms HAB^- and A^{2-} may vary, their sum (defined as the "total acid concentration" C_a is a constant for a particular solution:

$$C_a = [H_2A] + [HA^-] + [A^{2-}]$$

Charge balance: The solution may not possess a net electrical charge:

$$[H_3O^+] = [OH^-] + [HA^-] + 2[A^{2-}]$$

> Why do we multiply $[A^{2-}]$ by 2? Two moles of H_3O^+ are needed in order to balance out the charge of 1 mole of A^{2-}.

Simplified treatment of polyprotic acid solutions

The calculations shown in this section are all you need for the polyprotic acid problems encountered in most first-year college chemistry courses. More advanced courses may require the more exact methods in Lesson 7.

Because the successive equilibrium constants for most of the weak polyprotic acids we ordinarily deal with diminish by several orders of magnitude, we can usually get away with considering only the first ionization step. To the extent that this is true, there is nothing really new to learn here. However, without getting into a lot of complicated arithmetic, we can often go farther and estimate the additional quantity of H^+ produced by the second ionization step.

> ✔ Example 13.3.14: **Solution of CO$_2$ in water**
>
> *a)* Calculate the pH of a 0.050 *M* solution of CO_2 in water.
>
> For H_2CO_3, $K_1 = 10^{-6.4} = 4.5E-7$, $K_2 = 10^{-10.3} = 1.0E-14$.
>
> b) Estimate the concentration of carbonate ion CO_3^{2-} in the solution.
>
> ***Solution***

a) Because K_1 and K_2 differ by almost four orders of magnitude, we will initially neglect the second dissociation step. Because this latter step produces only a tiny additional concentration of H⁺, we can assume that [H⁺] = [HCO₃⁻] = x:

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{(x)^2}{.050 - x} = 4.5 \times 10^{-7} \quad \text{(i)}$$

Can we further simplify this expression by dropping the *x* in the denominator? Let's try:

$x = [0.05 \times (4.5E\text{–}7)]^{\frac{1}{2}} = 1.5E\text{–}4$.

Applying the "5-percent test", the quotient x/C_a must not exceed 0.05. Working this out yields (1.5E–4)/(.05) = .003, so we can avoid a quadratic.
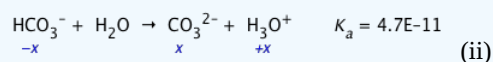
$x = [H^+] \approx (K_a C_a)^{\frac{1}{2}} = [(4.5E\text{–}7) \times .01]^{\frac{1}{2}} = (.001)^{\frac{1}{2}} = 0.032$ M,

and the

pH = – log .032 = **1.5**.

b) We now wish to estimate $[CO_3^{2-}] \equiv x$.

Examining the second dissociation step, it is evident that this will consume *x* mol/L of HCO₃⁻, and produce an equivalent amount of H⁺ which adds to the quantity we calculated in *(a)*.

$$HCO_3^- + H_2O \rightarrow CO_3^{2-} + H_3O^+ \qquad K_a = 4.7E\text{-}11$$
$$\quad -x \qquad\qquad\quad x \qquad +x \qquad\qquad\qquad \text{(ii)}$$

Owing to the very small value of K_2 compared to K_1, we can assume that the concentrations of HCO₃⁻ and H⁺ produced in the first dissociation step will not be significantly altered in this step. This allows us to simplify the equilibrium constant expression and solve directly for $[CO_3^{2-}]$:

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{(x + 1.5E\text{-}4)\,x}{(1.5E\text{-}4) - x} \approx \frac{(1.5E\text{-}4)\,x}{(1.5E\text{-}4)} = x = 4.7E\text{-}11 \quad \text{(iii)}$$

It is of course no coincidence that this estimate of $[CO_3^{2-}]$ yields a value identical with K_2; this is entirely a consequence of the simplifying assumptions we have made. Nevertheless, as long as $K_2 \ll K_1$ and the solution is not highly dilute, the result will be sufficiently accurate for most purposes.

## Sulfuric acid: A Special Case

Although this is a strong acid, it is also diprotic, and in its second dissociation step it acts as a weak acid. Because sulfuric acid is so widely employed both in the laboratory and industry, it is useful to examine the result of taking its second dissociation into consideration.

✔ Example 13.3.1: Solution of H₂SO₄

Estimate the pH of a 0.010 M solution of H_2SO_4 with $K_1 = 10^3$ and $K_2 = 0.012$

Solution:

Because $K_1 > 1$, we can assume that a solution of this acid will be completely dissociated into H_3O^+ and bisulfite ions HSO_4^-. Thus the only equilibrium we need to consider is the dissociation of a 0.010 M solution of bisulfite ions.

$$HSO_4^- + H_2O \rightarrow SO_4^{2-} + H_3O^+$$

$$K_2 = \frac{[H^+]\left[SO_4^{2-}\right]}{[HSO_4^-]} = \frac{(x)^2}{.010 - x} = 0.012$$
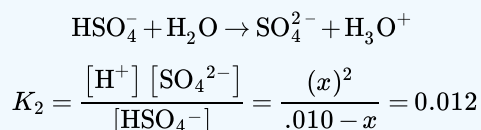
Setting $[H^+] = [SO_4^{2-}] = x$, and dropping x from the denominator, yields

$$x \approx \sqrt{(0.010)(0.012)} = \sqrt{1.2 \times 10^{-4}} = 0.0011$$

Applying the "five percent rule", we find that x / C_a = .0011/.01 = .11 which is far over the allowable error, so we must proceed with the quadratic form. Rewriting the equilibrium expression in polynomial form gives

$$x^2 + 0.022x - 1.2 \times 10^{-4} = 0$$

Inserting the coefficients {1 .022 .000012} into a quad-solver utility yields the roots 4.5×10^{-3} and -0.0027. Taking the positive root, we obtain

$$pH = -\log(0.0045) = 2.3$$

Thus the second "ionization" of H_2SO_4 has only reduced the pH of the solution by 0.1 unit from the value (2.0) it would theoretically have if only the first step were considered.

Amino acids and Zwitterions

Zwitterions: molecular hermaphrodites

Amino acids, the building blocks of proteins, contain amino groups $-NH_2$ that can accept protons, and carboxyl groups $-COOH$ that can lose protons. Under certain conditions, these events can occur simultaneously, so that the resulting molecule becomes a "double ion" which goes by its German name *Zwitterion*.

Glycine: the simplest amino acid

The simplest of the twenty natural amino acids that occur in proteins is *glycine* $H_2N–CH_2–COOH$, which we use as an example here.
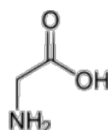
glycine

Solutions of glycine are distributed between the acidic-, zwitterion-, and basic species:
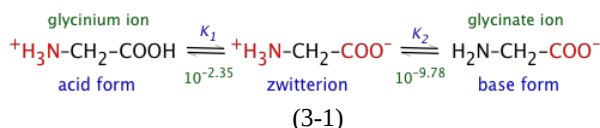

(3-1)

Figure: Although the zwitterionic species is amphiprotic, it differs from a typical ampholyte such as HCO_3^- in that it is electrically neutral owing to the cancellation of the opposite electrical charges on the amino and carboxyl groups.

In the following development, we use the abbreviations H_2Gly^+ (glycinium), HGly (zwitterion), and Gly^- (glycinate) to denote the dissolved forms.

The two acidity constants are

$$K_1 = \frac{[H^+][HGly]}{[H_2Gly^+]} = 10^{-2.25} \tag{13.3.13}$$

and

$$K_2 = \frac{[H^+][Gly^-]}{[HGly]} = 10^{-9.78} \tag{13.3.14}$$

If glycine is dissolved in water, charge balance requires that

$$H_2Gly^+ + [H^+] \rightleftharpoons [Gly^-] + [OH^-] \tag{13.3.15}$$

Substituting the equilibrium constant expressions (including that for the autoprotolysis of water) into the above relation yields

$$\frac{[H^+][HGly]}{K_1} + [H^+] = \frac{K_2[HGly]}{[H^+]} + \frac{K_w}{[H^+]} \tag{13.3.16}$$

✔ Example 13.3.3: Glycine solution speciation

Calculate the pH and the concentrations of the various species in a 0.100 M solution of glycine.

Solution

Substitution into Eq 4 above yields

$$[\mathrm{H^+}] = \sqrt{\frac{10^{-9.8} \times 0.10 + 10^{-14}}{0.1 / \left(10^{-2.3} + 1\right)}} = 10^{-6.1} \tag{i}$$

The concentrations of the acid and base forms are found from their respective equilibrium constant expressions (Eqs 2):

$$\left[\mathrm{H_2 Gly^+}\right] = \frac{\left[\mathrm{H^+}\right] \times 0.10}{10^{-2.3}} = 10^{-4.7} \tag{ii}$$

$$\left[\mathrm{Gly^-}\right] = \frac{10^{-9.8} \times 0.10}{\left[\mathrm{H^+}\right]} = 10^{-4.7} \tag{iii}$$

The small concentrations of these singly-charged species in relation to $C_a = 0.10$ shows that the zwitterion is the only significant glycine species in the solution.

If Equations ii and iii in this Example are recalculated for a range of pH values, one can plot the concentrations of each species against pH for 0.10 M glycine in water:
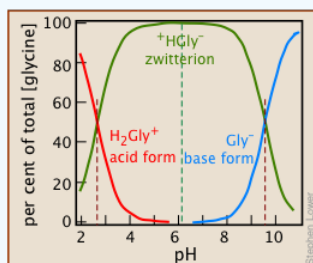
This distribution diagram shows that the zwitterion is the predominant species between pH values corresponding to the two pKas given in Eq 3-1.

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